Synthesis of Nanocrystalline Magnesium Ferrites Powder from Mill Scale

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Abstract -**Nano-crystalline magnesium ferrites powder were synthesized using mill scale via classical ceramic route. The effect of annealing temperature and Mg:Fe molar ratios (0.5, 0.55 and 0.65) on the formation of $MgFe_2O_4$ were studied. The results showed that the mole ratio of Mg/Fe and the annealing temperature were factors affecting the formation of $MgFe_2O_4$ in pure form. The magnesium ferrite formed were accompanied by a percentage of the iron oxide for the Mg:Fe = 0.5 and 0.55 for all studied annealing temperatures. The presence of iron oxide is very high at annealing temperature 1000°C and highly decreased with the raise of annealing temperature. A single phase of $MgFe_2O_4$ was formed at Mg:Fe=0.65 at 1200 °C. The nanocrystalline size of the prepared $MgFe_2O_4$ phase prepared was in the range of 170nm had good magnetic properties with maximum saturation magnetization (36.64 emu/g) at Mg/Fe mole ratio 0.65 and 1300°C.**

Keywords-***mill scale; magnesium ferrite; nanocrystalline; ceramic route***

I. INTRODUCTION

The ferrite material is a new advanced material which characterized by high magnetic permeability, high saturation magnetization and low power losses. These materials are extensively used in magnetic fluid, microwaves devices, magnetic recording media, and fabrication of radio frequency coils, transformer cores, and chock coils, noise filters, recording heading and rod antennas [1-3]. Mg ferrites belong to the normal, or the inverse, spinel structure ferrites group. Magnesium ferrite ($MgFe_2O_4$) has a cubic spinel-type structure [4, 5]. It is well known as -a soft magnetic n-type semiconductive material, with high resistivity and low magnetic and dielectric losses. These materials are extensively used in magnetic fluid, microwaves devices, magnetic recording media, and fabrication of radio frequency coils, transformer cores, and chock coils, noise filters, recording heading and rod antennas. In addition, Mg ferrites are very important in heterogeneous catalysis, adsorption and sensors [6, 7].

The magnetic properties of the ferrites depend on the microstructure [8, 9]. The microstructure of the ferrite is determined by a variety of factors; raw materials quality, annealing temperature, annealing time and the materials composition. This fact is very important because the microstructures developed during sintering are determined, to a large extent, by the powder's characteristics (crystallite size and shape, size distribution, porosity, state of agglomeration, chemical and phase composition), which are closely associated with the processing method [8, 9]. However, there is no many studies has been found in the literature correlating the microstructure and effect of grain size with the magnetic properties of Mg ferrite powders. This study, therefore, will investigate the effect of the sintering temperature (1000 - 1300°C) on the microstructure and magnetic properties of $MgFe_2O_4$ ferrites prepared by ceramic method.

On the other hand, during the heating of steel slabs before rolling in the steel-making process, their upper layer can be oxidized to iron oxide. This oxide is called "mill scale", and it is easily removed from the surface by a shower of water during the rolling of these slabs [10-13]. This mill scale can be considered as a valuable secondary raw material according to its high iron content, low impurities and stable chemical composition. The quantity of mill scale is increasing rapidly with the current demand of increasing world steel production. The high iron content of these materials with its very low impurities makes it an excellent source for soft and hard magnets preparation via its mixing with other metal oxides and further heat treatment at various temperatures.

From this point of view, the present investigation handled an economic route for using the ceramic technique in synthesis of magnetic nano-crystalline magnesium ferrite powder through solid-state reaction of a mixture consisting of secondary iron oxide resources with analytical grade magnesium oxide in different Fe/Mg mole ratios. The effect of firing temperatures as well as firing time on both physical and magnetic properties of the produced compacts will investigated.

II. EXPERIMENTAL

This paper aimed to handle an economic route for using the conventional ceramic technique in synthesis of magnetic nano-crystalline magnesium ferrite powder as soft magnetic materials for industrial and different magnetic applications. A mill scale sample with 70.1% total iron, 46.5% Fe^{2+}, 21.6% Fe_3O_4, 0.44% metallic iron, 0.52% SiO_2, 0.18% CaO, 0.084% Al_2O_3, 0.029% MgO, 0.02% S and 0.21% C was obtained from HADEED Saudi Iron & Steel Company(SABIC). Mill scale fines were finely ground to a mean particle size of

0.074 mm and then thoroughly mixed with stoichiometric amount of analytical grade magnesium oxide. A series of mill scale and magnesium oxide with various Mg:Fe molar ratios (0.5, 0.55 and 0.65) were prepared. The pre-calculated stoichiometric ratios of mall scale and MgO were mixed in a ball for 6 h and then dried at 100℃ overnight. For the formation of the Mg ferrite phase, the dried precursors (powders were calcined at a rate of 10 ℃/min in static air atmosphere up to the required annealed temperature and maintained at the temperature for the annealing time in the muffle furnace. The effect of annealing temperature (1000, 1100, 1200 and 1300 ℃) on the formation of Mg ferrite was studied while the annealing time was constant and kept 2 hours.

The crystalline phases present in the different samples were identified by X-ray diffraction (XRD) on a Brucker axis D8 diffractometer using Cu-K_{α} (λ =1.5406) radiation and secondary monochromator in the range 2θ from 10° to 80°. The crystallite size of magnesium ferrite present in the investigated was based on X-ray diffraction line broadening and calculated using Scherrer equation. The ferrites particles morphologies were observed by scanning electron microscope (SEM, JSM-5400). The magnetic properties of the ferrites were measured at room temperature using a vibrating sample magnetometer (VSM; 9600-1 LDJ, USA) in a maximum applied field of 10 kOe. From the obtained hysteresis loops, the saturation magnetization (*Ms*) was determined

III. RESULTS AND DISCUSSIONS

A mill scale sample with 70.1% total iron obtained from HADEED Saudi Iron & Steel Company (SABIC) was used in this study to synthesized magnesium ferrite through conventional ceramic rout as soft magnetic material for industrial applications. A series of experiments was carried out at different annealing temperatures ranging from 1000 to 1300℃ for 2 h to explain the effect of annealing temperature and Mg:Fe mole ratios (0.5, 0.55 and 0.65) on the formation of $MgFe_2O_4$ powder prepared using the conventional solid-state method. Fig. 1 showed the XRD patterns of $MgFe_2O_4$ from mill scale and magnesium oxide precursor with Mg:Fe mole ratio 0.5 thermally treated at temperatures 1000, 1100, 1200 and 1300℃ for calcination time of 2 h. From the results, It is evident that at Mg:Fe mole ratio 0.5, the formation of single-phase $MgFe_2O_4$ could not be obtained at this mole ratio and contains impurity peaks of α-Fe_2O_3 phase. At a temperature of 1000℃, the $MgFe_2O_4$ ferrite phase formed contained large amounts of impurity, which were due to the α-Fe_2O_3 phase. It can be observed that the presence of $MgFe_2O_4$ phase and hematite phase are nearly equal ratio. At 1100℃, the hematite phase was highly decreased while the $MaFe_2O_4$ was highly formed. This could be observed from the lowering of the peak intensities of hematite peak. Behind the annealing temperature 1100℃, the annealing temperature has a limiting effect on the formation of $MgFe_2O_4$. At annealing temperatures 1200 and 1300℃, a slight decrease in the hematite phase was observed. It could be also observed that the peak intensities for the ferrite phase were increased with the increasing of annealing temperature up to 1200^0C and slightly decreased at annealing temperature 1300^0C. These results indicated that the Mg:Fe = 0.5 did not led to the formation of single phase of $MgFe_2O_4$. This limiting effect of annealing temperature was due to the limiting connection between magnesium oxide and the iron oxide in the precursor at this mole ratio.

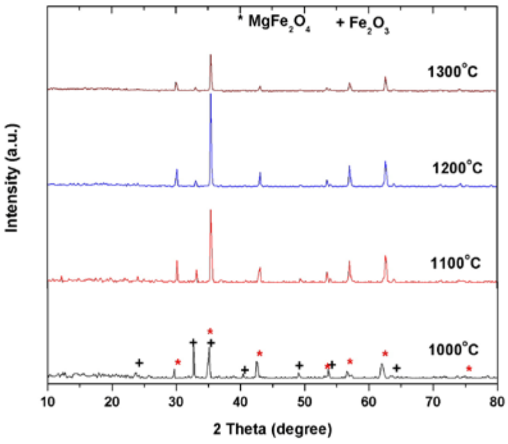

Fig. 1 XRD patterns of the $MgFe_2O_4$ powder produced at mole ratio of Mg:Fe = 0.5

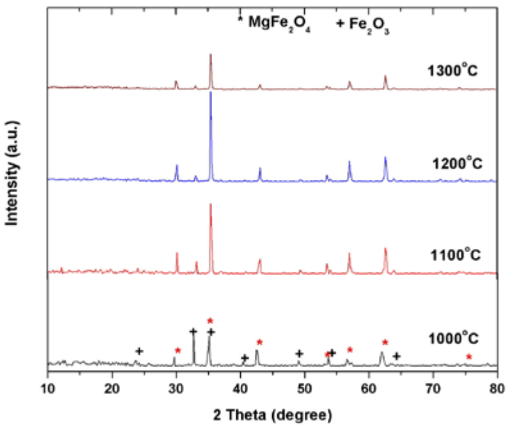

Fig. 2 XRD patterns of the MgFe2O4 powder produced at mole ratio of Mg:Fe = 0.55

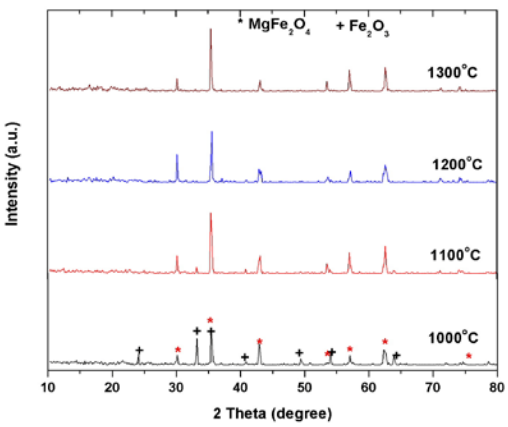

Fig. 3 XRD patterns of the MgFe2O4 powder produced at mole ratio of Mg:Fe = 0.65

Fig. 2 and 3 showed the XRD patterns of $MgFe_2O_4$ from mill scale and magnesium oxide precursor with Mg:Fe = 0.55 and 0.65, respectively, thermally treated at temperatures 1000, 1100, 1200 and 1300°C for calcination time of 2 h. As in Mg:Fe = 0.5, the $MgFe_2O_4$ ferrite phase formed contained large amounts of α-Fe_2O_3 phase at a temperature of 1000 °C and the presence of $MgFe_2O_4$ phase and hematite phase are almost equal ratios for both Mg:Fe = 0.55 and 0.65. This indicate that the Mg:Fe mole ratios had not strong effect on the formation of $MgFe_2O_4$ at low annealing temperature (1000^0C). As the annealing temperature increased to1100^oC, the formation of magnesium ferrite phase was highly enhanced for both the two Mg:Fe mole ratios. However, the Mg:Fe 0.55 did not led to the formation of single phase of $MgFe_2O_4$ at all annealing temperature (Fig. 2) while a single phase of $MgFe_2O_4$ was formed at annealing temperatures 1200 and 1300^0C for the precursor with Mg:Fe = 0.65 (Fig. 3). The peak intensities for the ferrite phase were increased with the increasing of annealing temperature up to 1200^0C and slightly decreased at annealing temperature 1300^0C for the two Mg:Fe mole ratios (Fig. 1-3).

The crystallite size of the produced magnesium ferrite phase for the most intense peak (3 1 1) was determined from the XRD data using the Debye–Scherrer formula. The crystalline size for the well-crystallized pure single $MgFe_2O_4$ phase was found to be increase by increasing the annealing temperature and depends on the Fe:Mg mole ratios. However, the crystalline sizes of 172 and 182 nm were obtained at 1200 and 1300 °C, respectively for Fe:Mg = 2:1.3.

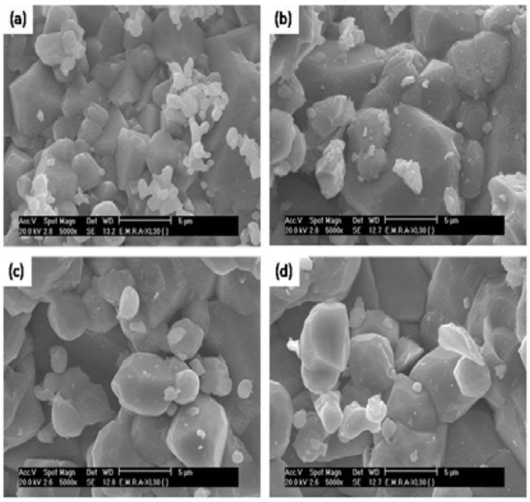

Fig. 4 SEM micrograph of the produced nanocrystalline MgFe2O4 powders prepared at: (a) Mg/Fe = 0.5 & 1200oC, (b) Mg/Fe = 0.5 & 1300oC, (c) Mg/Fe = 0.65 & 1200oC and (d) Mg/Fe = 0.65 & 1300oC

In order to investigate the influence of annealing temperature and Mg:Fe mole ratio on the morphology and microstructure of the prepared magnesium ferrite powder, further investigation was carried out by SEM and are shown in Fig. 4a-d. It is clear that there is an increase in grain size with raising annealing temperature. The SEM images of the powder synthesized from the mall scale and magnesium oxide with Mg:Fe = 0.5 and thermally treated at 1200°C for 2 h (Fig. 4a) showed irregular microstructures with spherical small particles in addition to the largest particles, indicating that the composition is insufficient for the complete formation of the structure. The presence of smaller grains can be attributed to no coarsened α-Fe_2O_3 existing in the annealed samples obtained at this Mg:Fe and this annealing temperature. The particles size of the formed ferrite was ranging from a diameter of 0.5 to 3.5 μm. For the powder with Mg:Fe = 0.5 and thermally treated at 1300°C (increase of annealing temperature), the ferrite powders possessed an uniform coarse structure with a well-clear crystalline microstructure containing a fewer numbers of spherical small particles as shown in Fig. 4b. It can be also observe that the grain size was larger than that observed at lower temperature .The average grain sizes for the powders annealed at 1300°C were about 1–6 μm. The clear and homogeneous microstructure become more pronounced for the sample with Mg:Fe = 0.65 annealed at 1200 and 1300°C, respectively, as shown in Fig. 4c and d. Moreover, the SEM micrographs showed that the spherical small particles were disappeared, which indicated that the Mg:Fe = 0.65 was sufficient to produce a single $MgFe_2O_4$ phase with homogeneous microstructure and a uniform size distribution with an average grain size of about 3 to 6 μm.

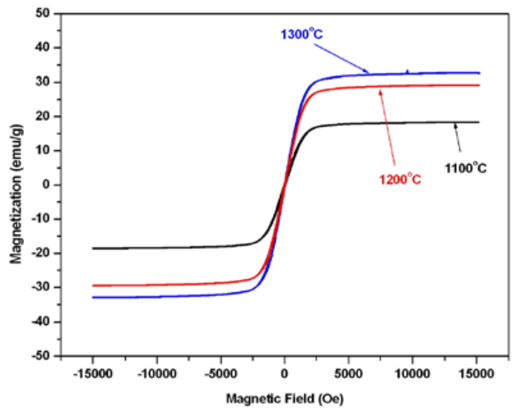

Fig. 5 Effect of annealing temperature on the M-H hysteresis loop of MgFe2O4 powders produced at mole ratio of Mg:Fe = 0. 5

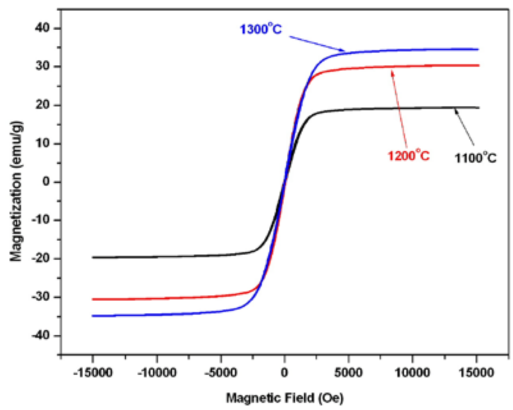

Fig. 6 Effect of annealing temperature on the M-H hysteresis loop of MgFe2O4 powders produced at mole ratio of Mg:Fe = 0. 55

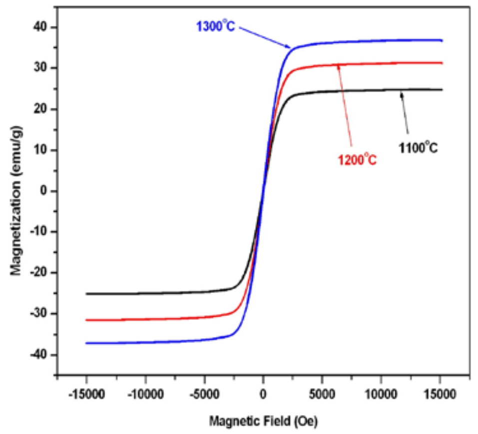

Fig. 7 Effect of annealing temperature on the M-H hysteresis loop of $MgFe_2O_4$ powders produced at mole ratio of Mg:Fe = 0. 65

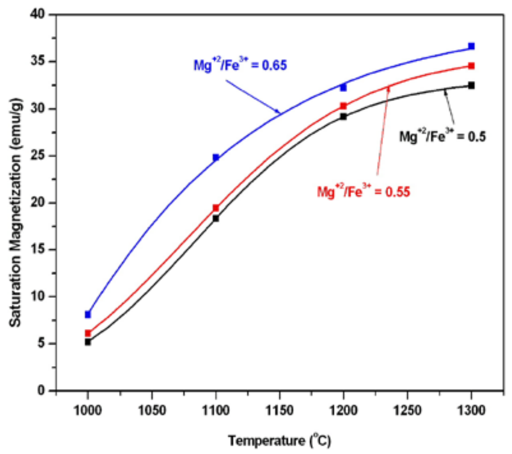

Fig.8 The saturation magnetization as a function of annealing temperature of MgFe5O8 for Mg/Fe =0.5, 0.55and 0.65 annealed for 2 h.

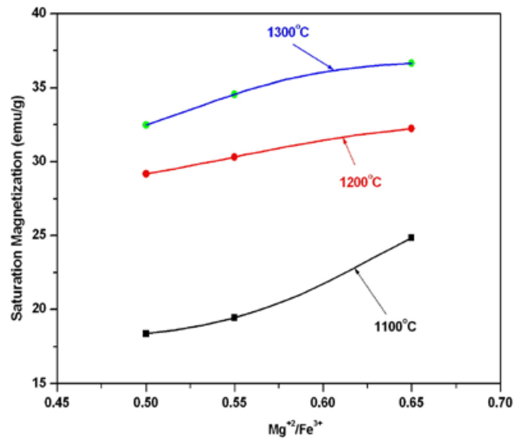

Fig.9 The saturation magnetization as a function of Mg/Fe mole ratio for annealing temperatures 1100-1300oC annealed for 2 h.

The magnetization of the produced magnesium ferrite powders was performed at room temperature under an applied field of 16 KOe and the hysteresis loops of the ferrite powders were obtained. Plots of magnetization (*M*) as a function of applied field (*H*) per Mg/Fe mole ratio and annealing temperature were shown in Figs 5 - 9. Figs. 5 - 7 showed the hysteresis measurements for the effect of annealing temperature (1100 -1300^{o}C) at Mg/Fe = 0.5, 0.55 and 0.65 respectively. Fig. 8 plotted the saturation magnetization as a function of annealing temperatures from 1100 to 1300^{o}C for all the Mg/Fe mole ratios (0.5, 0.55and 0.65) while Fig. 9 plotted the saturation magnetization as a function of Mg/Fe mole ratio for all the studied annealing temperature. In general, Fig. 5 and 7 indicated that the magnesium ferrite was a soft magnetic material due to the deviation from rectangular form and there very low coercivity and the magnetic properties of the prepared magnesium ferrites are strongly dependent on the Mg ion concentration and the annealing temperature. The results showed that the values of saturation magnetization of the Mg ferrite powders were increased by increasing the annealing temperature from 1100 to 1300^{o}C and which can be attributed to the increase in phase formation, sample grain size and crystalline sizes. The magnesium ferrite powders with Mg/Fe mole ratio 0.65 and annealed at 1300 C for 2 h exhibited an optimum saturation magnetization of 36.64emu/g. Such high saturation magnetization for Mg ferrite annealing at 1300◦C can be attributed to the high phase purity and well-defined crystallinity of $MgFe_5O_8$. Fig. 8 showed that the saturation magnetization increased steadily with increasing treatment temperature from 1100 to 1300^{o}C for the entire studied Mg/Fe mole ratios as results of increasing Mg ferrite formation. It exhibited a maximum value of magnetization at annealing temperature 1300^{o}C for 2 h. This is due to the presence of single phase of magnesium ferrite particles. The increase in the saturation magnetization by increasing the annealing temperature was due to the increase of phase purity and well-defined crystallinety of $MgFe_5O_8$. The saturation magnetization of the Mg ferrites powders increased continuously with the increase in Mg ion concentration up to Mg/Fe mole ratio 0.65 and at all annealing temperatures (1100-1300^{o}C) as shown in Figs. 9 and this can be attributed to the increase of the quantities of Mg ferrite formation. These results were in agreement with those observed in XRD results.

IV. CONCLUSIONS

Nanocrystalline magnesium ferrites were synthesized using secondary iron oxide “mill scale” produced from Hadeed Company (in KSA) which produced during the rolling of the steel slabs. The classical ceramic method was used for the preparation the magnesium ferrite. The results can be summarized as:

- A magnesium ion concentration was important to synthesize single-phase $MgFe_2O_4$ powder by economic ceramic route.
- A single- phase of nanocrystalline magnesium ferrite could not obtained a t Mg/Fe mole ratios 0.5 and 0.55 and contains impurity of α-Fe_2O_3 phase

A single phase of nanocrystalline $MgFe_2O_4$ was formed at the precursor with Mg/Fe mole ratios 0.65 at annealing temperature $\geq 1200^oC$.

- Samples that contains hematite as impurities showed irregular microstructures with spherical small particles
- The Mg/Fe mole ratios 0.65 was sufficient to produce a single $MgFe_2O_4$ phase with homogeneous microstructure and a uniform size distribution
- The nanocrystalline size of the prepared $MgFe_2O_4$ phase prepared by using co-precipitation methods was in the range of 170nm.
- The formed Mg ferrite powders had good magnetic properties with maximum saturation magnetization (36.64 emu/g) was achieved for the single phase at Mg/Fe mole ratio 0.65 and annealing temperature 1300^oC.

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